

Supporting Information:

Holey Graphene as a Weed Barrier for Molecules

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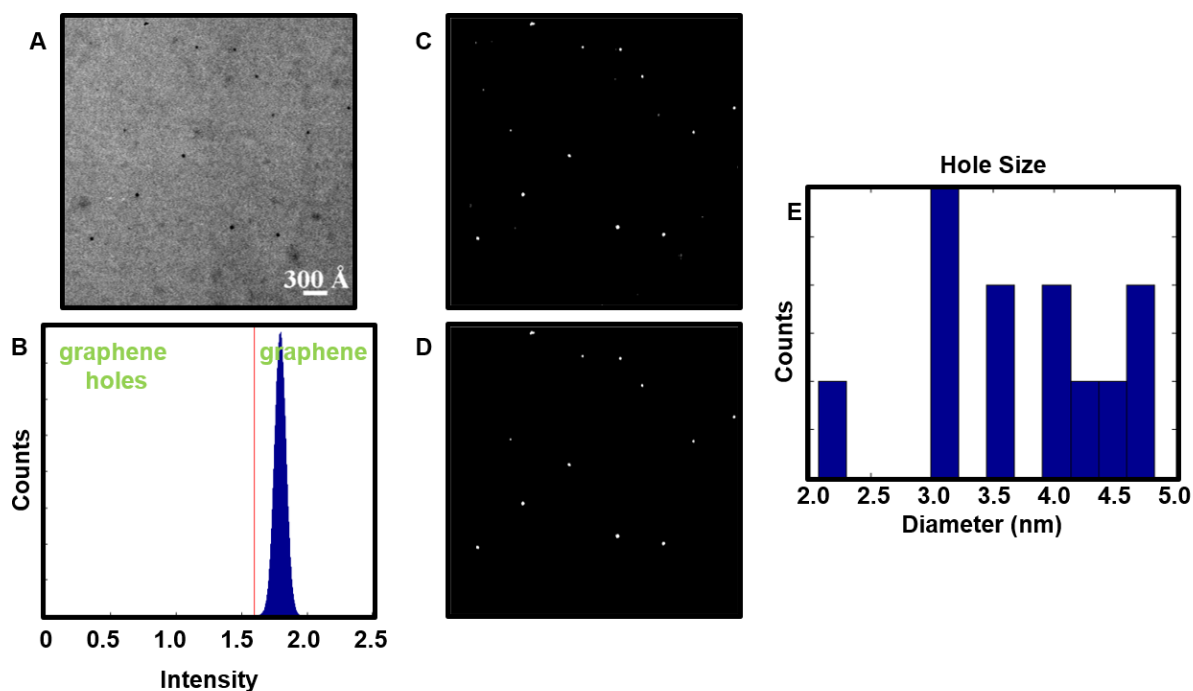


Figure S1. (A) Original transmission electron microscopy image from Figure 2 before segmentation. (B) An image histogram of the data in A showing the intensity threshold cut off used to create an image binary. (C) Resulting binary mask, where graphene holes are separated from the graphene layer. (D) Small outlier artifacts in the image binary are removed. (E) The diameters of the remaining holes are displayed in a bar graph, binned by diameter (10 Å bin width); we measure an average 37 ± 8 Å hole size.

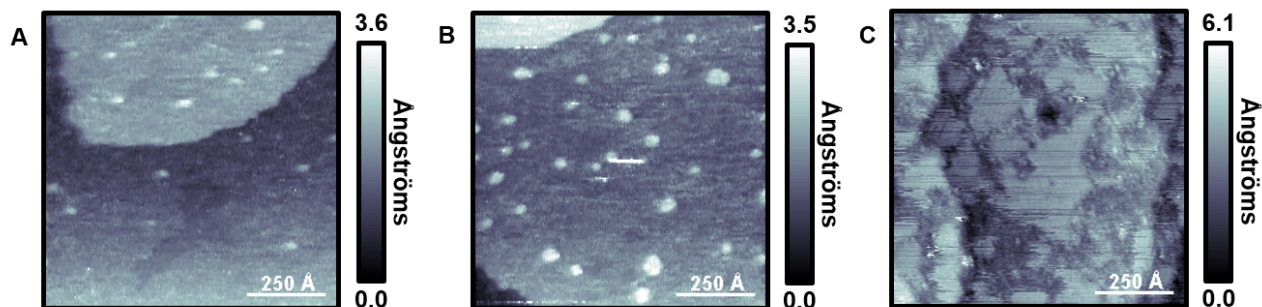


Figure S2. (A,B) Scanning tunneling micrographs ($I_{\text{tunneling}} = 3 \text{ pA}$, $V_{\text{sample}} = -1.0 \text{ V}$) of “holey” graphene on Au{111}/mica directly after deposition from solution of water and acetone. Images show protrusions and depressions, displayed as brighter and dimmer, respectively. We attribute the higher protrusions as solvent that has not desorbed from the holes, and depressions as holes (without solvent) within the graphene overlayer. (C) After annealing at 100 °C for 24 h, all solvent is evaporated and only the depressions (holes) remain.

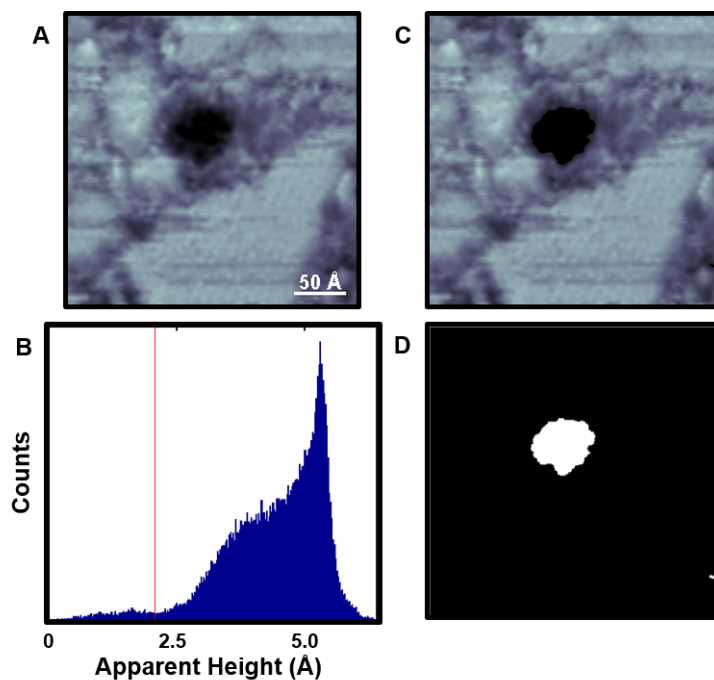


Figure S3. (A) Scanning tunneling micrograph ($I_{\text{tunneling}} = 3 \text{ pA}$, $V_{\text{sample}} = -1.0 \text{ V}$) of “holey” graphene on Au{111}/mica with (B) a corresponding apparent height histogram. Masking techniques, performed in MATLAB, enable “holey” regions and graphene regions to be isolated and analyzed independently. (C) The image in A is segmented by apparent height. The graphene layer is $2.1 \pm 1.2 \text{ Å}$ higher in average apparent height compared to (D) the exposed Au region.

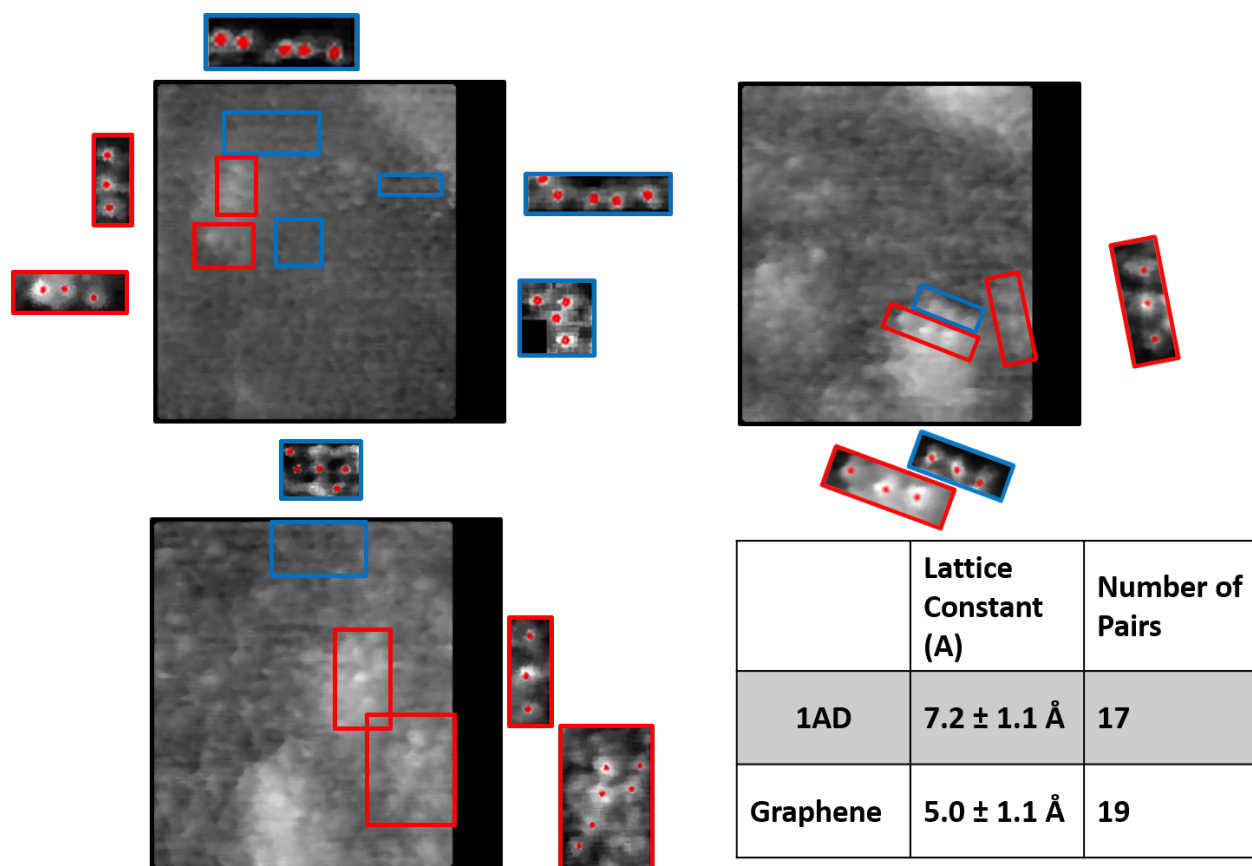


Figure S4. Scanning tunneling micrographs ($I_{\text{tunneling}} = 3 \text{ pA}$, $V_{\text{sample}} = -1.0 \text{ V}$) of “holey” graphene filled with 1-adamantanethiolate (1AD) on Au{111}/mica, where the spacing between adjacent 1AD molecules and graphene atoms is recorded. Images of the molecules were first smoothed and then analyzed using the Regionprops function in Matlab in the molecular regions highlighted. The inserted molecular layer shows an average spacing (across multiple images) of $7.2 \pm 1.1 \text{ Å}$, while the graphene mask shows an average spacing of $5.0 \pm 1.1 \text{ Å}$.

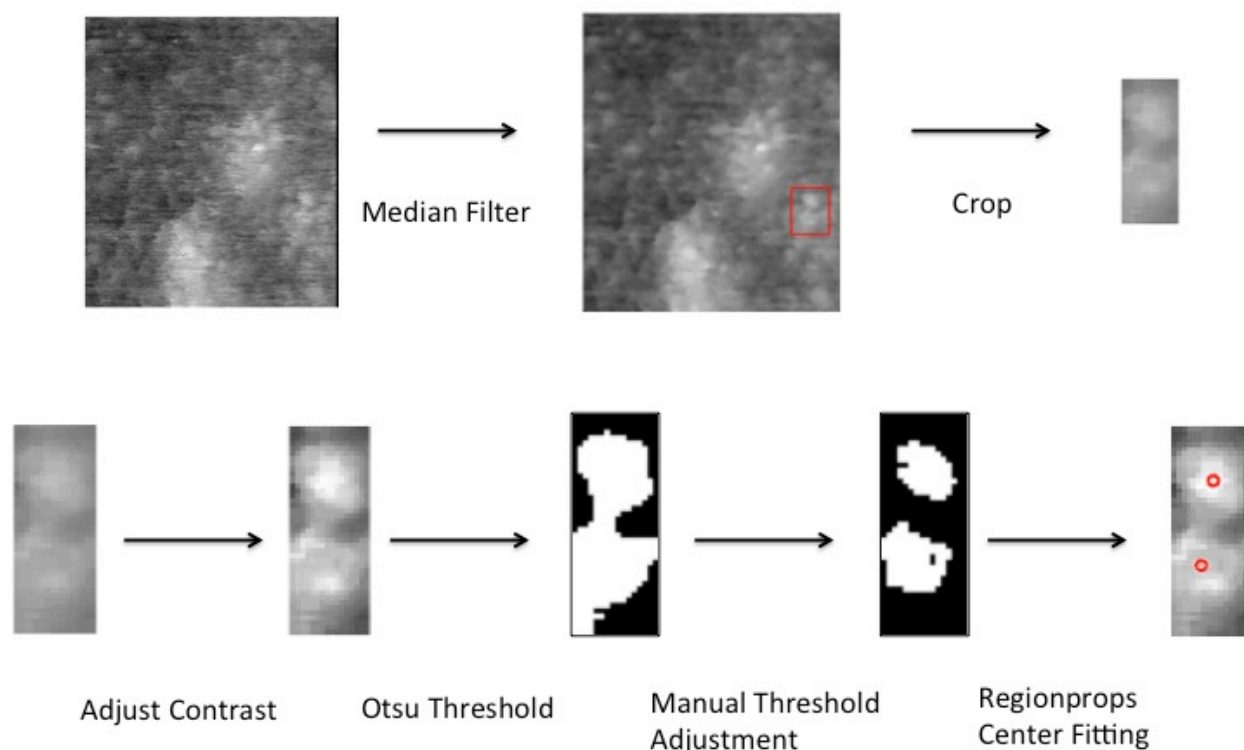


Figure S5. Molecule Fitting Methodology. To determine nearest-neighbor spacings between molecules post-1AD deposition, molecules were fit using the Regionprops function in Matlab. A median filter is applied to remove intensity spikes, and then the region of interest is cropped for analysis. The contrast of the cropped image is enhanced, and then the image is thresholded using the Otsu cutoff. The cutoff was increased until sufficient segmentation was achieved. The average adjustment was 0.16 where images were set to a grayscale. Finally, the center of each segmented molecule was determined. The locations of these centers were used to calculate nearest-neighbor distances. Fittings were also performed on regions that were analyzed in Fourier space to crosscheck results.

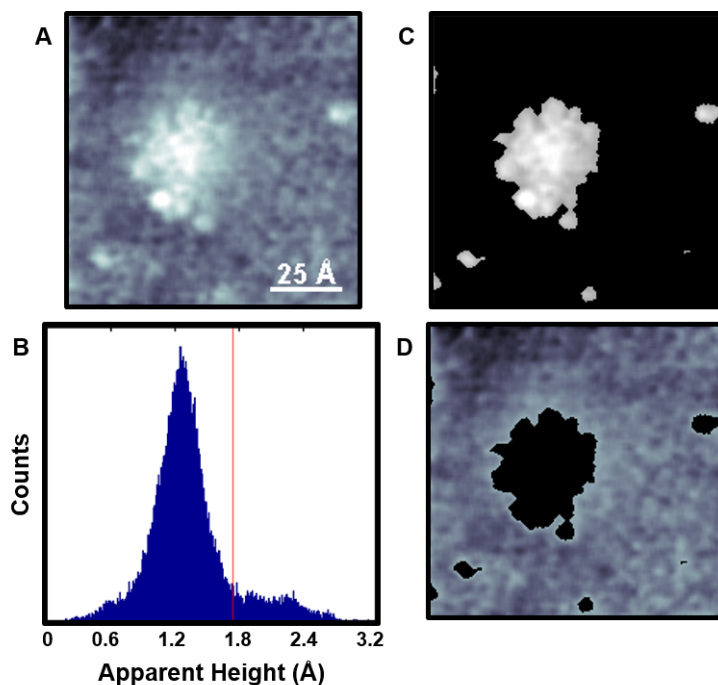


Figure S6. (A) Scanning tunneling micrograph ($I_{\text{tunneling}} = 3 \text{ pA}$, $V_{\text{sample}} = -1.0 \text{ V}$) of “holey” graphene filled with 1-adamantanethiolate on Au{111}/mica with (B) a corresponding apparent height histogram. Masking techniques, performed in MATLAB, enable filled regions and bare graphene regions to be isolated and analyzed independently. (C,D) The image in A is segmented by apparent height and displayed. A 1-admantanethiolate patch appears on average $1.1 \pm 0.5 \text{ Å}$ than the graphene layer.

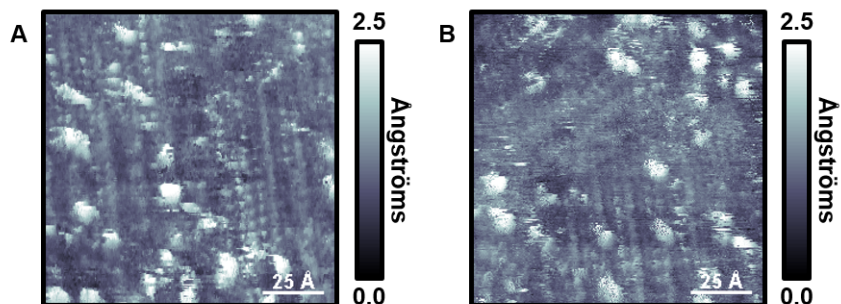


Figure S7. (A, B) Scanning tunneling micrographs ($I_{\text{tunneling}} = 3 \text{ pA}$, $V_{\text{sample}} = -1.0 \text{ V}$) of “holey” graphene on Au{111}/mica after a second 1-adamantanethiolate vapor deposition for 24 h. Each sample was regenerated, prior to the second deposition step, by annealing at $250 \text{ }^{\circ}\text{C}$. Images depict 1AD molecules within a “holey” graphene framework.